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ALTERNATIVE VIEWS ON ENTROPY MODELS AND STATISTICAL APPROACHES IN EXTENDED THERMODYNAMICS

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Abstract

Three formalisms are considered which challenge extended irreversible thermodynamics (EIT) or derivations thereof. One of these argues that we can control heat flow $\vec{Q}$ along a rigid conductor to make internal energy U depend only on temperature T in disagreement with EIT. However, such a process is forbidden in general by an exact equation for $\partial\vec{Q}/\partial t$. A second challenge argues that the Boltzmann entropy must be used in a dilute gas, equivalent to EIT with an infinity of variables, and that the Liouville equation cannot describe irreversibility. However, ROBERTSON has shown the Liouville equation to be consistent with irreversible linear heat conduction. LUZZI and VASCONCELLOS derive EIT approximately from a modified Liouville equation. The ROBERTSON formalism provides a tractable approach without their approximations.

Keywords: extended thermodynamics (EIT), objections to EIT, discussion of objections.

1. Introduction

Extended irreversible thermodynamics (EIT) [1]–[3] adds to the state variables of classical non-equilibrium thermodynamics [4] the dissipative fluxes of the classical formalism such as heat flux $\vec{Q}$, diffusion flow $\vec{J}_D$, traceless pressure, $\overset{\circ}{\mathbf{P}}$, and chemical reaction-rates. It postulates an entropy S dependent on a finite set of variables, specifically all those whose values can be extracted from a given experiment. These variables obey rate equations which, taken together with the hydrodynamic conservation equations, predict $\mathrm{d}S/\mathrm{d}t \geq 0$ for an irreversible process in an isolated system.

An exact derivation form the Liouville equation of conservation and rate equations, together constituting 'generalized hydrodynamic equations', has been given by ROBERTSON [5] for the classical case and has been generalized [6] to apply to the extended regime. Let $\sigma(x,t)$ [5] be a distribution dependent on time t and phase co-ordinates x which JAYNES [7] has determined to maximize the information-theoretic $S = -\mathrm{Tr}\,(\sigma \ln \sigma)$ subject to $\eta_i = \mathrm{Tr}\,\{\sigma F_i(x)\}$ $(1 \leq i \leq \nu)$, where $\{F_i(x)\}$ are a set of phase functions whose averages are the variables $\{\eta\}$ in

the extended scheme. ROBERTSON [5] has derived via projection operators from the Liouville equation an exact equation for $\partial\sigma/\partial t$ whose moments yield an exact closed set of equations for $\{\dot{\eta}_i\}$. Here 'exact' implies that all variables are included for which empirical information is available; the Jaynesian $\sigma(x,t)$, together with the moment equations, solves exactly the equation for $\partial\sigma/\partial t$. Statistical derivations of the extended rate equations yield, in the classical limit, correlation expressions for linear and non-linear transport coefficients.

To cast the generalized hydrodynamic equations in the form of phenomenological equations of EIT, one expresses rates $\{\dot{\eta}_i\}$ in terms of thermodynamic forces $\beta^{-1}\lambda_i \equiv -\partial F/\partial\eta_i$, where $F = U - TS$ is the Helmholtz function, and $U = \mathrm{Tr}\,(\sigma\hat{H})$, with $\hat{H}$ the Hamiltonian. In a non-uniform system, all variables and functions F_i vary with position $\vec{r}$, and derivatives are functional derivatives. In doing this [6], we take the information-theoretic S to be a model for non-equilibrium thermodynamic entropy. This entropy model obeys a standard Gibbs equation [8]. The information-theoretic entropy model may well not be unique, and the possibility of using other models opens the way to variant formalisms which we discuss here. One class of objection [9] finds a process which EIT forbids and argues that it should be allowed. This argument restricts the variables on which E and S depend, leading to a modification of EIT. Another objection [10] arises because projection operators are abstract and formal, so that it is difficult to prove the increasing entropy principle in general. It is proposed [11] that the Boltzmann entropy must be used in a dilute gas and, in more general systems, the Gibbs entropy rather than the entropy of EIT which depends on time only through its dependence on a set of time-dependent variables $\{\eta_i\}$. Then the Liouville equation must be modified to make the Boltzmann H-theorem follow exactly form it. The third approach [12, 13] uses the information-theoretic entropy model but asserts that there is a preferred set of variables. Otherwise we need a closure approximation. In this approach, the derivation of equations for the time-dependence of the variables uses a propagation function of ZUBAREV [14] which has questionable information-theoretic roots and solves the Liouville equation exactly only if the latter is modified by adding source terms. Here, we examine each of these successively in the light which the ROBERTSON formalism [5, 6] sheds on them.

2. Thought Experiment of Bhalekar and Garcia-Colin

First we look at the arguments of BHALEKAR [9] who considers heat flow along a rigid heat conductor of length L with temperature $T(x,t)$ at x $(0 \le x \le L)$; $T_1 \equiv T(0,t)$; $T_2 \equiv T(L,t)$; and $T_1 > T_2$. Vaguely developed reasoning leads the author to conclude that T_1 and T_2 can be controlled so that heat flux $Q(x,t)$ obeys

$$\partial Q/\partial x \equiv \omega(x), \qquad (0 \le x \le L), \tag{1a}$$

$$Q(x,t) = \psi(x) + Q_0(t). \tag{1b}$$

Thus $\partial Q/\partial x$ depends only on x, and we obtain (1b) by integrating (1a) from 0 to x. ψ is the integral of ω, and $Q_0 = Q(0, t)$.

If we consider the system to be a small volume V centred at x, then the energy conservation equation for internal energy density U/V asserts that

$$(\partial/\partial t)(U/V) = -\partial Q/\partial x = -\omega(x). \tag{2}$$

A time integration of (2) yields

$$U/V = -\omega(x)t + E_1(x), \tag{3}$$

where $E_1(x)$ is a constant of the t-integration. BHALEKAR asserts [9] that since U/V does not depend on $Q_0(t)$, it does not depend on Q, which disagrees, in general, with EIT. From the Gibbs equation of EIT, $\partial U/\partial Q = T\partial S/\partial Q - F_Q$, where F_Q, proportional in linear heat conduction to Q, is the thermodynamic force associated with the variable Q. From the integrability condition for the Helmholtz function, F, $\partial S/\partial Q = \partial F_q/\partial T$. Then $\partial U/\partial Q$ is proportional to Q unless F_Q is proportional to T, but not otherwise T-dependent, and U has a contribution $O(Q^2)$. BHALEKAR proposes a modified extended thermodynamics [9, 15] called 'Generalized Phenomenological Irreversible Thermodynamic Theory' (GPITT). In the latter formalism, S and U depend on T and on a set of additional parameters which have no rôle in rigid heat conduction. In that case, both are functions only of T.

To test these conclusions, we remark that the ROBERTSON formalism [5, 6] derives a set of generalized hydrodynamic equations which depend only on statistical and mechanical properties and not at all on assumptions about entropy. A model for thermodynamic entropy is needed only when conservation and rate equations are expressed in terms of thermodynamic forces. With Q and T the variables, the equation for $\partial Q/\partial t$ is the CATTANEO–VERNOTTE equation,

$$\partial Q/\partial t = -\{1/\tau(T)\}Q - \Gamma(T)\partial T/\partial x. \tag{4}$$

Explicit t-dependence of τ disappears after a short time [16]. *Eq.* (4) is also well established on phenomenological grounds [17, 18] because it leads to a hyperbolic equation for $T(x, t)$, removing the classical anomaly of solution which admits of infinite propagation velocity. An equation very similar to (4) arises in the BHALEKAR formalism (ref. [15], *Eq.* IV–8) as a generalized Gibbs–Duhem equation, but he makes no use of it to test (1a,1b).

To see whether (1a,1b) is compatible with both (2) and (4), expand $\omega(x)$ and $E_1(x)$ in powers of x and $Q_0(t)$ in powers of t and substitute into (2) and (4). In general, the right-hand member of (4) contains $O(x^p t^q)$ for all p, q. If we go to order n in the t and x expansions, the number of terms kept in (4) would be of order n^2 whereas the adjustable coefficients in $\omega(x)$, $E_1(x)$, and $Q_0(t)$ would be of order $3n$ unless $\tau(T)$, $\Gamma(T)$ have vanishing T-derivatives. If τ and Γ are T-independent, the adjustable parameters can be determined to satisfy (4), and then EIT does not forbid the BHALEKAR process. Where the process is incompatible

with (4), taking U to be Q-independent does not alter this conclusion. Usually, the T-dependences of τ and Γ are neglected. Where this dependence is negligible, experimental attempts to investigate realizability of the BHALEKAR process where EIT forbids it are likely to be difficult.

3. Non-Equilibrium Thermodynamics Based on Boltzmann Entropy

A second approach based on an entropy differing from that of EIT starts from the Boltzmann entropy, S_B, of kinetic theory. In a dilute gas, the momentum distribution at point $\vec{r}$ is $f(\vec{r}, \vec{p}, t)$. In terms of this, the entropy density at $\vec{r}$ is defined to be

$$S_B - \kappa \int f[\ln f - 1]\,\mathrm{d}\vec{p}. \tag{5}$$

If f is expanded as an infinite sum of Hermite functions, with coefficients which depend on the moments of f which can be chosen as independent variables, as proposed by GRAD [19], then S_B has an infinite number of independent arguments. In a typical experiment in which we measure only a small number of moments, S_B is not determined uniquely by the measurements, as is the entropy in EIT.

S_B satisfies exactly the H-theorem. This has the form of the Clausius–Duhem equation,

$$\partial S_B/\partial t = -\nabla \cdot \vec{J}_S + \sigma_S, \qquad \sigma_s \geq 0, \tag{6}$$

where $\vec{J}_S$ is the entropy flux, if f obeys exactly the kinetic theory Boltzmann equation, assuming binary collisions and molecular chaos. It is argued [20] that (6) is a 'thermodynamic law', so that in a formalism based on 'thermodynamic laws', S_B must represent the entropy. Since (6) is not exact consequence of the Liouville equation, it follows that the latter must be modified if it is to be consistent with the putative 'thermodynamic laws' governing irreversibility. Since the Gibbs entropy $S_G = -\int \rho \ln \rho \,\mathrm{d}x$ reduces at high dilution to a result proportional to the configuration integral of S_B, S_G must be the entropy for non-dilute systems. However, the Liouville equation implies $\mathrm{d}S_G/\mathrm{d}t = 0$ for any process having a finite rate in an isolated system. We are led to conclude that the Liouville equation must be modified through addition of a term which will make $\mathrm{d}S_G/\mathrm{d}t$ consistent with (6) at high dilution.

This reasoning contradicts the projection operator results of ZWANZIG [22] and ROBERTSON [23] which purport to derive irreversible thermodynamics from the Liouville equation. ROBERTSON has shown [23] that irreversible entropy production is ≥ 0 for linear heat conduction if we write $(-1/\tau)Q = LF_Q$ in (4) as derived from his formalism and have $L > 0$. It has long been difficult to calculate L which involves projection operators. However, this has been done recently [16] for ROBERTSON formalism, giving an L consistent with the fluctuation-dissipation theorem expression for thermal conductivity. We have evidence, therefore that, for $t > 0$, the unmodified Liouville equation can describe an irreversible process.

If we accept the assertion that 'thermodynamic laws' require that S_B represent entropy in a dilute system and choose the moments of f as independent variables, it has been shown [24] that this expression for S_B in terms of moments, together with (6), are equivalent to an EIT with an infinite set of state variables. This would imply that we can use EIT with a small set of measurable variables only if the remaining variables are irrelevant.

Such a conclusion contradicts ROBERTSON [5] who derives an EIT with information-theoretic entropy and arbitrary number of variables. GRMELA [25] has argued that different levels of description which successively become increasingly macroscopic are applicable to successive stages in the approach to equilibrium starting in a dilute system with (5) and (6) where there are an infinite number of variables. EIT is an intermediate stage, i.e. more macroscopic. All these stages fit a common Landau–Ginzburg equation. The idea that only the highest level is possible does not fit into this picture.

Finally, we consider a formalism [12, 13] which derives non-linear EIT, with information-theoretic entropy, from the Liouville equation and does not use projection operators. However, this is done only within approximations whose importance is hard to assess. One sets $\hat{H} = \hat{H}_o + \hat{H}$, where $\hat{H}_o$ governs very rapid relaxation processes. One chooses a set of n operators $\hat{P}_j$ whose averages are dynamical variables, so that

$$(ih)^{-1}[\hat{P}_j, \hat{H}_o] = \sum_{k=1}^{n} \Omega_{jk} \hat{P}_k \qquad (1 \leq j \leq n). \tag{7}$$

A set $\{\hat{P}_j\}$ satisfying this closed set of n equations are a preferred set. Otherwise commutators generate operators not in the set, and one needs a closure approximation.

The time-dependence of a variable is given by $P(t) = \lim_{\varepsilon \to 0} \mathrm{Tr}(\hat{P}\rho_\varepsilon)$, where following ZUBAREV [14], ρ_ε is an exact solution of a Liouville equation containing a source term $0(\varepsilon)$. $\rho_\varepsilon(t)$ looks like the information-theoretic distribution we should have if we took data over an interval during which we do not actually take any. The information basis is not clear. Complexity of the calculations means that quantitative results are few, although the formalism may be useful for semiconductor plasmas for which it was designed. The ROBERTSON formalism, despite its projection operators which we now have ways [16] of handling, is simpler as a general justification of EIT.

Whilst it is simple and convenient to take the information-theoretic $-\kappa \mathrm{Tr}(\sigma \ln \sigma)$ as a model for thermodynamic entropy, there may well be an infinite number of such models in non-equilibrium as in equilibrium. Disagreement among them, e.g. as to number of variables, is not a proof that any of them must be wrong. The foregoing discussion is designed to defend EIT or its derivation from an unmodified Liouville equation by showing that the three theories examined do not present conclusive arguments for the need to use the formalisms they propose.

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